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DESCRIPTION

RESIN COMPOSITION AND USE THEREOF

5 TECHNICAL FIELD

The present invention relates to a resin composition comprising a polylactic acid resin and a polyalkylene carbonate and to a use thereof. More particularly, the present invention relates to a resin composition comprising
 10 a polylactic acid resin and a polyalkylene carbonate, which is excellent in properties, such as flexibility, transparency, heat resistance and gas barrier properties, and which, after use, exhibits degradability in natural environment, and relates to a use thereof.

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BACKGROUND ART

Soft polyvinyl chloride, soft polyvinylidene chloride, polypropylene, polyethylene and the like are generally known as resins having flexibility and having high transparency
 20 and heat resistance.

However, these resins, when disposed of after use, increase the volume of refuse, and are further scarcely decomposed in natural environment with the result that, when buried, the resins semipermanently remain in the earth.

On the other hand, for example, a polylactic acid and
5 a copolymer of polylactic acid and other aliphatic polyester
(hereinafter referred to as "polylactic acids") and a
polyester derived from an aliphatic polyhydric alcohol and
an aliphatic polycarboxylic acid have been developed as
biodegradable resins.

Among these biodegradable resins, expansion of the application field of the polylactic acids is especially expected because they have excellent properties such as high rigidity, and L-lactic acid which is the starting material thereof comes to be manufactured in a large amount with reduced cost by the fermentation process.

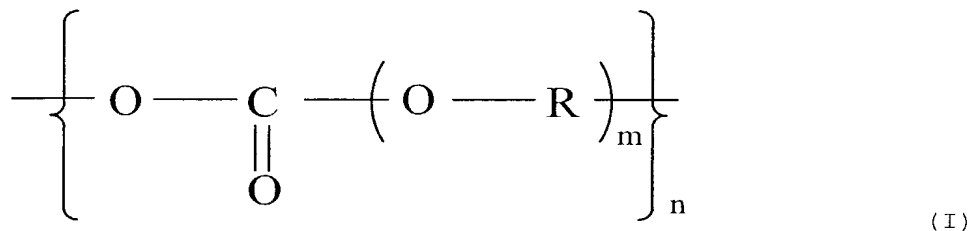
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prolonged reaction time, so that the method has a disadvantage of lacking simplicity.

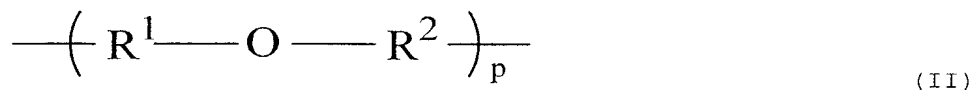
Therefore, there is a demand for the development of a resin composition enhanced in flexibility containing a biodegradable resin such as a polylactic acid, which exhibits enhanced gas barrier properties without detriment to the excellent properties of biodegradable resin, and is free from the occurrence of bleedout with the passage of time.

In these circumstances, the inventor has made extensive and intensive investigations. As a result, it has been found that a resin comprising a biodegradable polylactic acid resin and a specified polyalkylene carbonate is biodegradable and is excellent in properties such as flexibility. The present invention has been completed on the basis of this finding.

Japanese Patent Laid-open Publication No. 6(1994)-345956 discloses a resin composition comprising a polyethylene carbonate, and a synthetic polymer that is degraded by microorganism, such as poly(3-hydroxybutyric acid) or polycaprolactone, and/or a natural polymer, such as starch, which is indicated as highly biodegradable. However, satisfactory attention was not paid to the transparency which is an important property for packing materials such as a film. Further, Japanese Patent



wherein R represents at least one group selected from the group consisting of an ethylene group, a propylene group and a group of the general formula (II):



(wherein each of R^1 and R^2 independently represents an alkylene group having 2 to 6 carbon atoms; and p is an integer of 1 to 15);

m is an integer of 1 to 15; and

n is an integer of 3 to 15,000.

It is preferred that the resin composition of the present invention comprise:

40 to 90 parts by weight of the biodegradable polylactic acid resin (A), and

60 to 10 parts by weight of the polyalkylene carbonate (B), providing that the sum of components (A) and (B) is 100 parts by weight, and

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satisfying that a pressed film of 0.1 mm thickness formed therefrom has a haze of 40% or less.

In the present invention, it is preferred that the polyalkylene carbonate (B) be polyethylene carbonate.

5 The resin composition preferably satisfies that a pressed film of 0.5 mm thickness formed therefrom has a Young's modulus at 23°C of 2500 MPa or less.

Also, preferably, the resin composition satisfies that a pressed film of 0.1 mm thickness formed therefrom has a
10 carbon dioxide permeability coefficient at 25°C of 85 cc mm/m² day atm or less.

The above resin composition of the present invention is preferably employed in the production of a molded article, such as a film, an oriented film, an injection-molded product,
15 a blow-molded product, a laminate, a tape, a nonwoven fabric or a yarn.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in detail below.

20 The resin composition of the present invention comprises a biodegradable polylactic acid resin (A) and a polyalkylene carbonate (B). First, each of these components will be described.

Biodegradable polylactic acid resin (A)

Examples of the lactic acids include L-lactic acid, D-lactic acid, DL-lactic acid and mixtures thereof and further include lactides which are cyclic dimers of lactic acids.

15 Examples of the aliphatic polyhydric alcohols used in
combination with lactic acids include ethylene glycol,
diethylene glycol, triethylene glycol, polyethylene glycol,
propylene glycol, dipropylene glycol, 1,3-butanediol,
1,4-butanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol,
20 1,9-nonanediol, neopentyl glycol, polytetramethylene
glycol, 1,4-cyclohexanedimethanol and
1,4-benzenedimethanol.

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Specific embodiments of copolylactic acids which can preferably be employed in the present invention include the followings:

(1) lactic acid block copolymer prepared from 50% by weight or more of lactic acid and 50% by weight or less of caproic acid,

(2) lactic acid block copolymer prepared from 50% by weight or more of lactic acid and 50% by weight or less of 1,4-butanediol and succinic acid,

(3) block copolymer comprising 50% by weight or more of polylactic acid segments and 50% by weight or less of polycaproic acid segments, and

(4) block copolymer comprising 50% by weight or more of polylactic acid segments and 50% by weight or less of polybutylene succinate segments.

In the present invention, lactic acid homopolymer or a block copolymer comprising polylactic acid segments and polybutylene succinate segments and/or polycaproic acid segments can especially preferably be used as the polylactic acid resin.

The weight average molecular weight (M_w) and molecular weight distribution of polylactic acid resins preferably employed in the present invention are not particularly

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(wherein each of R^1 and R^2 independently represents an alkylene group having 2 to 6 carbon atoms; and p is an integer of 1 to 15);

5 m is an integer of 1 to 15, preferably 1 to 10; and
n is an integer of 3 to 15,000, preferably 10 to 10,000.

With respect to the group represented by the above general formula (II), it is preferred that p be an integer of 1 or 2. Preferred examples include the groups of the
10 formula (II) wherein P is 1, such as 3-oxapentanylene, 3-oxahexanylene, 3-oxaheptanylene, 3-oxa-1-methylpentanylene and 3-oxa-1-methylhexanylene groups.

With respect to the polyalkylene carbonate (B) for use
15 in the present invention, the alkylene group represented by R in the above formula (I) may contain an alkylene group other than the ethylene group, propylene group and group of the general formula (II) in an amount not detrimental to the characteristics of the present invention, preferably
20 an amount not exceeding 20 mol% of the alkylene groups. Examples of such other alkylene groups include saturated aliphatic groups such as methylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene,

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The film for measuring haze is obtained by a process comprising first satisfactorily drying a resin composition, interposing a given amount thereof between two brass plates, aluminum plates and mold release films, subsequently melting
5 the resin composition at 200°C, compressing the molten resin composition under 10 MPa for 1 min and thereafter subjecting the same to 10 MPa compression and cooling by means of a compression molding machine set for 0°C so as to form a 100 μm thick film.

10 This film preferably exhibits a carbon dioxide permeability coefficient at 25°C of 85 cc mm/m² day atm or less, more preferably 80 cc mm/m² day atm or less, and optimally 75 cc mm/m² day atm or less.

Sheets formed from the resin composition of the present
15 invention preferably exhibit a Young's modulus at 23°C of 2500 MPa or less, more preferably 2200 to 50 MPa, and optimally 2000 to 100 MPa.

The sheet for measuring Young's modulus is obtained by a process comprising first satisfactorily drying a resin
20 composition, interposing a given amount thereof between two brass plates, aluminum plates and mold release films, subsequently melting the resin composition at 200°C, compressing the molten resin composition under 10 MPa for 1 min and thereafter subjecting the same to 10 MPa compression

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and cooling by means of a compression molding machine set for 0°C so as to form a 500 μm thick sheet.

The process for producing the resin composition of the present invention is not particularly limited, and common
5 processes for producing a resin composition comprising a thermoplastic resin can appropriately be employed.

For example, the process wherein the polylactic acid resin (A) such as the above-mentioned polylactic acid resin and the polyalkylene carbonate (B) are homogeneously mixed
10 together by means of a high-speed agitator or a low-speed agitator and thereafter melt kneaded by means of a single screw or multiscrew extruder having satisfactory kneading capacity can be employed. Also, the process wherein raw materials in solid form are mixed together by means of, for
15 example, a Henschel mixer or a ribbon blender can be employed. Further, the process of kneading and melting polymers, by means of, for example, an extruder can be employed. Moreover, the process wherein heating and melting are performed in a reaction vessel equipped with a vacuum device and an
20 agitator, followed by kneading under ordinary pressure or in vacuum, can be employed. Of these processes, it is preferred in the present invention that the resin composition is prepared by the process wherein raw materials having

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mixed together in solid form are melt kneaded by means of a twin-screw extruder at 180 to 220°C.

The resin composition produced by the above processes, although may be in any of forms such as pellets, rods and powder, is preferably taken out in the form of pellets.

The obtained resin composition can be further subjected to a solid state polymerization. The solid state polymerization removes volatile low molecules from the resin composition and increases the molecular weight. The solid state polymerization can be accomplished, for example, by first heating satisfactorily predried resin composition pellets in a stream of inert gas, such as nitrogen gas, at 60 to 120°C for 10 to 180 min so as to effect crystallization, and thereafter heating the resin composition pellets in a stream of inert gas, such as nitrogen gas, or in vacuum at 90 to 150°C for 0.5 to 200 hr.

The resin composition of the present invention may be loaded with various stabilizers, an ultraviolet absorber, a flame retarder, an internal mold release agent, a lubricant, a plasticizer, an organic filler, an inorganic filler, a pigment, a pigment dispersant and the like in conformity with intended use. Appropriate addition of these enables fabricating molded articles having desirable properties,

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(3) Blow molding (injection blow molding, stretch blow molding or direct blow molding)

For example, in the injection blow molding, pellets of the resin composition of the present invention are melted
 5 and charged into a metal mold by the use of common injection blow molding machine. Thus, preforms are obtained. Blow molded bottles are produced by reheating obtained preforms in an oven (furnace), placing them in a metal mold whose temperature is maintained at room temperature or below (-10
 10 to 20°C), and feeding compressed air to thereby effect blowing.

(4) Vacuum forming or vacuum air-pressure forming

Film or sheet preforms are produced in the same manner as in the above extrusion (1). Molded articles can be
 15 obtained by heating obtained preforms to thereby soften them and thereafter performing a vacuum forming or vacuum air-pressure forming thereof in a metal mold whose temperature is maintained at room temperature or below (-10 to 20°C) by the use of common vacuum forming machine.

20 (5) Lamination forming

In the lamination forming, a laminate can be obtained by any of the following methods;

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store, a cup for Chinese vermicelli, a cup as used in an automatic drink vending machine, a container or tray for food such as fresh fish, meat, vegetable, fruit, bean curd or daily dish, a truck box as used in a fresh fish market, 5 a container for dairy product such as milk, yogurt or lactic acid beverage, a container for carbonated drink or other refreshing drink, a container for alcoholic drink such as beer or whisky, a cosmetic container, a detergent container, a bleacher container, a cool box, a flowerpot, a tape, a 10 cushion material for use in transportation of an electrification product such as a television set or stereo equipment, a cushion material for use in transportation of a precision appliance such as a computer, a printer or a time piece, a cushion material for use in transportation 15 of an optical device such as a camera, spectacles, a microscope or a telescope, a cushion material for use in transportation of a ceramic product such as glass or ceramic ware, a shade material, a heat insulating material or a soundproofing material.

20 Also, the foam comprising the resin composition of the present invention is suitable for medical or sanitary purposes. For example, the foam can find appropriate application in a bandage, a carrier for dermal or mucosal patch agent, a triangular bandage, an adhesive plaster, a

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synthetic/artificial hide, a synthetic/artificial fur, a synthetic/artificial suede, a synthetic/artificial leather and network pipes.

Also, the textiles obtained by processing the resin composition of the present invention are suitable for medical or sanitary purposes. For example, the textiles can find appropriate application in a suture for surgical operation, a bandage, a triangular bandage, an adhesive plaster, a towel, a disposable towel, a disposable wet towel, an office roll towel, a hand towel, a duster, a tissue paper, a wet tissue paper for cleaning or disinfection, a wet tissue paper for baby hip wiping, a disposable diaper, a disinfected cotton, a sanitary or menstrual napkin, a sanitary tampon, an underpad, a blood absorbent tampon for operation or child birth, a sanitary cover stock material, a sterile bag, a kitchen refuse net, a garbage bag, etc.

In the same manner as described above with respect to the foam, these medical and sanitary products can be subjected to sterilization, pasteurization or disinfection, followed by sterile packaging. Further, products can be produced and packaged in sterile or endotoxin-free conditions in the same manner as described above with respect to the foam.

Still further, the textiles obtained by processing the resin composition of the present invention can be appropriately used in general industries including agriculture, fishery, forestry, manufacturing, construction, civil engineering, transportation and traffic, and recreation activities including leisure and sports. For example, the textiles can find appropriate application in an agricultural cheese cloth, a net against insect and bird, a sieve, a fishing line, a fishing net, a casting net, a spreading net, an oil absorbent material, a net, a rope, a climbing rope, a sail, a hood, a tarpaulin, a Tycon, a container bag, an industrial transit bag, a cement bag, a fertilizer bag, a filter material, a water permeable cloth for reclamation, a reinforcement cloth for soft ground, an artificial leather, a felt for paper making, a lining for flexible disk, a tent, a soil bag, a planting net, a heat insulating material, a soundproofing material, a shade material, a shock eliminator material, a cushion material, a binding material, a nonskid material for muddy and snow-covered roads, network pipes, a drainage pipe for civil engineering and construction, etc.

EFFECT OF THE INVENTION

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A 100 μm thick film was molded under given conditions and held at 110°C for 40 min. A sample in the form of a strip of 2 mm width and 2 cm length was cut out therefrom. A creep test of the sample was carried out by the use of
5 TMA (manufactured by Seiko Instruments Inc.) under a stress of 0.1 MPa in a nitrogen stream with the ambient temperature raised at a rate of 2 °C/min. Heat resistance was evaluated by the temperature at which the strain became 10% or greater. Evaluation criteria are as follows:

10 A : exceeding 140°C, B : 140 to 90°C, and C : lower than 90°C.

(5) Gas barrier property (carbon dioxide permeability coefficient)

With respect to a 100 μm thick film obtained in a given
15 manner, the carbon dioxide permeability properties were evaluated. The carbon dioxide permeability coefficient at 25°C was measured by the use of gas permeability coefficient meter GPM-250 (manufactured by GL Science). Smaller permeability coefficient value means higher gas barrier
20 properties.

(6) Evaluation of degradability

A sheet of 500 μm thickness and 3 cm x 3 cm size was formed, and buried in a compost of 58°C and 60% by weight water content (components: rice hulls, kitchen refuse,

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poultry manure, excrement, etc.). The degradability of the sheet was observed.

A : degradation was observed within 180 days, and

C : degradation was not observed.

5 (7) Water vapor barrier property of film

With respect to an about 20 μm thick cast film obtained in a given manner, the water vapor permeability rate was measured at 25°C in a relative humidity of 100%. The water vapor barrier property was evaluated by the value converted
10 in terms of a relative humidity of 90%. The smaller the value, the higher the water vapor barrier property.

(8) Tensile strength, elongation, flexural strength and flexural modulus of dumbbell specimen

Specimens obtained in a given manner were evaluated
15 in accordance with ASTM D-790.

(9) Drop impact test

A 1000 ml container obtained in a given manner was charged with 800 ml of water, and dropped in a 20°C atmosphere from a height of 1.5 m onto a concrete floor surface. The
20 dropping was repeated until the container was broken, and the number of droppings performed until breakage was recorded. No further dropping was performed upon completion of 10 droppings.

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Example 1

A glass reactor equipped with an agitator and a distillation tube was charged with 70 parts by weight of polylactic acid (Lacea H-100, produced by Mitsui Chemicals, Inc.) and 30 parts by weight of polyethylene carbonate (measured glass transition temperature: 13°C and weight average molecular weight: 151,000). The distillation tube was connected to a vacuum device including a vacuum pump and a vacuum regulator, and had such a structure that evaporated matter could be distilled off.

The reactor was heated to 120°C, and inner pressure thereof was reduced to 1 torr, and then, held in that condition for 4 hr to thereby remove water from the resins. Subsequently, the pressure was returned to atmospheric pressure, and the reaction system was heated to 210°C. Thereafter, the resins were mixed in a nitrogen atmosphere of 50 torr for about 1 hr and 30 min. The pressure within the reaction system was returned to atmospheric pressure, and resin composition (A1) was taken out.

The thus obtained resin composition (A1) was satisfactorily dried, and a given amount thereof was interposed between two brass plates, aluminum plates and mold release films. The resin composition was melted at 200°C, compressed under 10 MPa for 1 min, and further subjected

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to cooling and compression under 10 MPa by means of a compression molding machine set for 0°C. In this manner, a 0.5 mm thick sheet and a 100 µm thick film were obtained. The thus obtained sheet and film were evaluated with respect
 5 to the transparency, flexibility, heat resistance, gas barrier properties and degradability. The evaluation results are shown in Table 1.

Example 2

10 Resin composition (A2) was produced in the same manner as in Example 1, except that the amounts of charged polylactic acid and polyethylene carbonate were changed to 60 parts by weight of polylactic acid and 40 parts by weight of polyethylene carbonate. The resin composition was molded
 15 and evaluated in the same manner as in Example 1, and the evaluation results are shown in Table 1.

Example 3

20 Resin composition (A3) was produced in the same manner as in Example 1, except that the amounts of charged polylactic acid and polyethylene carbonate were changed to 50 parts by weight of polylactic acid and 50 parts by weight of polyethylene carbonate. The resin composition was molded

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and evaluated in the same manner as in Example 1, and the evaluation results are shown in Table 1.

Example 4

5 Resin composition (A4) was produced in the same manner as in Example 1, except that the amounts of charged polylactic acid and polyethylene carbonate were changed to 40 parts by weight of polylactic acid and 60 parts by weight of polyethylene carbonate. The resin composition was molded
10 and evaluated in the same manner as in Example 1, and the evaluation results are shown in Table 1.

Example 5

70 parts by weight of the same polylactic acid as used
15 in Example 1 and 30 parts by weight of the same polyethylene carbonate as used in Example 1 were dried by means of a vacuum dryer at room temperature for 48 hr. The dried resins were mixed by means of the laboplastomill (manufactured by Toyo Seiki Co., Ltd.) having a cylinder temperature set at 200°C
20 for 15 min, thereby obtaining resin composition (A5). The resin composition was molded and evaluated in the same manner as in Example 1, and the evaluation results are shown in Table 1.

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Comparative Example 1

100 parts by weight of the same polylactic acid as used in Example 1 only was subjected to the same molding and evaluation as performed in Example 1. The evaluation results are shown in Table 1.

Comparative Example 2

70 parts by weight of the same polylactic acid as used in Example 1 and 30 parts by weight of polycaprolactone (Celgreen RH-7, produced by Daicel Chemical Industries, Ltd.) in place of the polyethylene carbonate were mixed in the same manner as in Example 1, thereby obtaining resin composition (B1). The resin composition was molded and evaluated in the same manner as in Example 1, and the evaluation results are shown in Table 1. The resin composition, although being excellent in flexibility, exhibited poor transparency and poor gas barrier properties.

Comparative Example 3

100 parts by weight of the same polyethylene carbonate as used in Example 1 only was subjected to the same molding and evaluation as performed in Example 1. The evaluation results are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 1	Comp. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6
PLA*1 (pts.wt)	70	60	50	40	70	100	70	0			
PEC*2 (pts.wt)	30	40	50	60	30	0		100	50	20	50
PCL*3 (pts.wt)							30				
PHB*4 (pts.wt)									50	80	
PPL*5 (pts.wt)											50
mixing method*6	method Amethod	Amethod	Amethod	Amethod	Amethod B	-	method A	-	method B	method B	method A
transparency haze(%)	3	7	8	9	8	3	62	4	62	62	64
flexibility (MPa)	1890	1520	1180	660	1870	2650	1820	40	470	2550	11
heat resistance	A	A	A	B	A	A	A	C	A	A	C
gas barrier property	60	44	25	18	63	90	250	4.2	25	26	19
PCO ₂ (cc mm/m ² day atm)											
degradability	A	A	A	A	A	A	A	A	A	A	A

PLA*1: polylactic acid PEC*2: polyethylene carbonate PCL*3: polycaprolactone

PHB*4: poly(3-hydroxybutyric acid) PPL*5: polypropiolactone

mixing method*6: method A = mixed in reaction vessel for 1 hr and 30 min method B = mixed in laboplastomill for 15 min method C = mixed by twin screw extruder

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Example 6

80 parts by weight of satisfactorily dried polylactic acid and 20 parts by weight of polyethylene carbonate were blended by means of 30 mm-diameter twin screw extruder (manufactured by Plastic Kogyo Kenkyusho) at a cylinder temperature of 210°C, thereby obtaining resin composition (A6). The resin composition was evaluated in the same manner as in Example 1. Thereafter, the resin composition was kneaded, melted and extruded by means of a 20 mm-diameter extruder equipped with a T-die at a cylinder temperature of 190°C. The extrudate was cooled by means of rolls set for 20°C. Thus, a 20 μ m thick cast film was obtained. The moldability of the resin composition was excellent, and the obtained film was transparent and flexible. With respect to the film, the water vapor permeability property was evaluated. The evaluation results are shown in Table 2.

Examples 7 to 12

Mixing, molding and evaluation were performed in the same manner as in Example 6, except that the amounts of compounded components were as shown in Table 2. The evaluation results are shown in Table 2.

Comparative Example 7

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With respect to polylactic acid alone, an evaluation was effected in the same manner as in Example 6. The film was harder than in Examples 7 to 12, and the water vapor barrier property thereof was inferior to those of the

5 Examples.

Table 2

	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comp. Ex. 7
PLA*1 (pts.wt)	80	70	60	55	50	45	40	100
PEC*2 (pts.wt)	20	30	40	45	50	55	60	
mixing method*6	method C	method C	method C	method C	method C	method C	method C	-
transparency haze (%)	4	3	3	5	6	8	8	3
flexibility (MPa)	2050	1480	1400	1390	1300	1030	610	2650
heat resistance	A	A	A	A	A	A	B	A
gas barrier property	81	63	49	37	24	21	16	90
PCO ₂ (cc mm/m ² day atm)								
degradability	A	A	A	A	A	A	A	A
water vapor barrier property of film (25°C 90% RH: g mm/m ² day)	3.5	3.2	2.5	2.3	2.2	2.5	2.2	4.1

PLA*1: polylactic acid PEC*2: polyethylene carbonate
mixing method*6: method A = mixed in reaction vessel for 1 hr and 30 min method B = mixed in laboplastomill for 15 min method C = mixed by twin screw extruder

